Thermal conductivity of the thermoelectric layered cobalt oxides measured by the Harman method

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In-plane thermal conductivity of the thermoelectric layered cobalt oxides has been measured using the Harman method, in which thermal conductivity is obtained from temperature gradient induced by applied current. We have found that the charge reservoir block (the block other than the CoO_2 block) dominates the thermal conduction, where a nano-block integration concept is effective for material design. We have further found that the thermal conductivity shows a small but finite in-plane anisotropy between a and b axes, which can be ascribed to the misfit structure.

Thermoelectric materials have recently attracted a renewed interest as a energy-conversion material in harmony with our environments. They are characterized by the dimensionless figure of merit $ZT = S^2 T / \rho \kappa$, where S, ρ and κ are the thermopower, resistivity and thermal conductivity at temperature T, respectively. In other words, the thermoelectric material is a material that shows large thermopower, low resistivity and low thermal conductivity simultanously.

Oxides were regarded as unsuitable for thermoelectrics, but the layered cobalt oxides have been extensively investigated as a promising thermoelectric material since the discovery of a large thermopower in $NaCo_2O_4$ ($Na_{0.5}CoO_2$) [1, 2]. Soon after, the related layered cobalt oxides $Bi_{2-x}Pb_xSr_2Co_2O_y$ [3, 4], $Ca_3Co_4O_9$ [5, 6, 7], $Ca_2(Cu,Co)_2Co_4O_9$ [8] $TlSr_2Co_2O_y$ [9], and $(Pb,Co)Sr_2Co_2O_y$ [10] have been synthesized and identified. They share the hexagonal CdI_2-type CoO_2 block as a common unit as shown in Fig. 1, and show good ther-

moelectricity of $ZT > 1$ above 1000 K [11, 12, 13]. This means that their thermoelectric performance is comparable with that of the conventional thermoelectric materials such as PbTe and $Si_{1-x}Ge_x$.

Single crystals of the thermoelectric layered cobalt oxides are very thin and small, and the heat loss is too serious to measure κ precisely. There are only a few reports on κ measurement of single crystals, all of which were done above room temperature [11, 12, 13]. Fujita et al. [11] found that the in-plane thermal conductivity κ of a Na_xCoO_2 single crystal was 200 mW/cmK at room temperature, and decreased rapidly at high temperatures. This is highly inconsistent with the other layered cobalt oxides [12, 13] and the polycrystalline $NaCo_2O_4$ [14, 15], which needs cross-checking by other technique. We have succeeded in measuring in-plane κ of single crystals of Na_xCoO_2, $Bi_{2-x}Pb_xSr_2Co_2O_y$ and $Ca_3Co_4O_9$ by the Harman method. Here we will report on the experimental details of the Harman method and the in-plane κ of the layered cobalt oxides below room temperature.

$Bi_{2-x}Pb_xSr_2Co_2O_y$ single crystals were grown by a traveling-solvent floating-zone method [16]. Single crystals of Na_xCoO_2 and $Ca_3Co_4O_9$ were grown by the flux technique [1, 13]. A typical dimension of the samples was $2.0 \times 0.5 \times 0.05$ mm^3. Detailed growth conditions and charge transport were given in the cited references.

Thermal conductivity was measured in a closed-cycle refrigerator from 15 to 300 K by the Harman method, where κ was obtained from temperature difference induced by applied current I_0. Figure 2 shows the experimental configuration. This is similar to a four-probe method, but instead of the voltage terminals, two sets of chromel-constantan thermocouple are pasted to detect the temperatures T_L and T_R, and the difference $\Delta T = T_R - T_L$. The sample is hung with current leads (gold wire of 20μm-diameter) in vacuum, and is nearly isolated thermally. Then heat absorption/radiation due to the Peltier effect induced by I_0 balances a heat back-
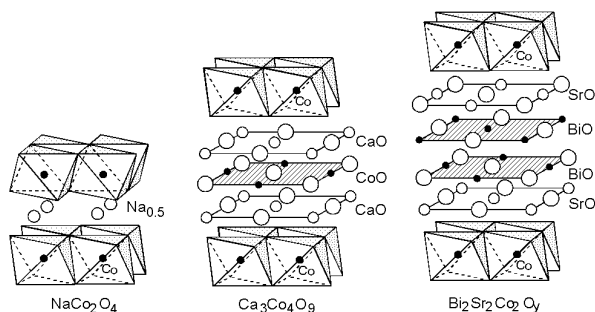

FIG. 1: Crystal structure of the layered cobalt oxides.

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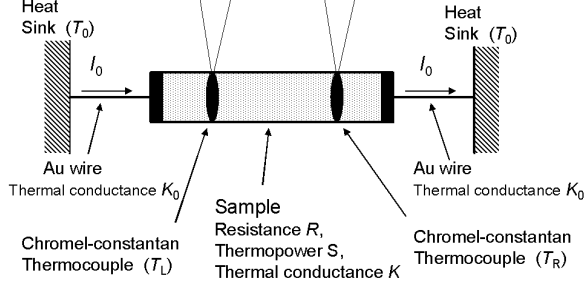
FIG. 2: The sample configuration of the Harman method.

flow across the sample, and in a steady state,

$$STI_0 = K\Delta T \qquad (1)$$

is realized. Thus the thermal conductance K is obtained from S (measured in advance in a different run), T and ΔT. In a steady-state method, κ is obtained from ΔT induced by applied thermal current. Since there is no "constant thermal current source", the measured κ always has some uncertainty coming from the contact thermal resistance. In contrast, we can use "constant current source" for I_0 in the Harman method, which is free from the contact thermal resistance like a four-terminal method for resistance measurement.

Now we will evaluate the heat loss from current wires. For simplicity, let us assume that the thermocouples are pasted just on the edges of the sample. Then, in a steady-state, the thermal-current balance on the left edge is written as

$$ST_L I_0 = K\Delta T + I_0^2 R/2 + K_0(T_0 - T_L), \qquad (2)$$

where R is the resistance (including the contact resistance), T_0 is the temperature at the heat sink, and K_0 is the thermal conductance of the wire. Here we take the current direction to give $T_R > T_L$ for $+I_0$. Similarly, the thermal-current balance on the right edge is written as

$$ST_R I_0 = K\Delta T + K_0(T_R - T_0) - I_0^2 R/2. \qquad (3)$$

Then we get

$$I_0^2 R + SI_0\Delta T = 2K_0(\bar{T} - T_0), \qquad (4)$$

$$S\bar{T}I_0 = (K + K_0/2)\Delta T, \qquad (5)$$

where $\bar{T} = (T_R + T_L)/2$. These equations mean that K and K_0 are simultaneously determined by measuring S, R, T_L and T_R. In our setup, K_0 was estimated to be 2×10^{-5} W/K by calculating a thermal conductance of a gold wire with a 20-μm diameter and a 10-mm long at 300 K. This was consistent with the values obtained through Eq. (4) from the measured values of T_L, T_R and T_0, and was subtracted at every measurement. We evaluated the radiation loss to be 6×10^{-6} W/K at 300 K through the Stefan-Boltzmann law. Since a typical value of K is 3-5×10^{-4} W/K, we can safely neglect the contribution of the radiation loss.
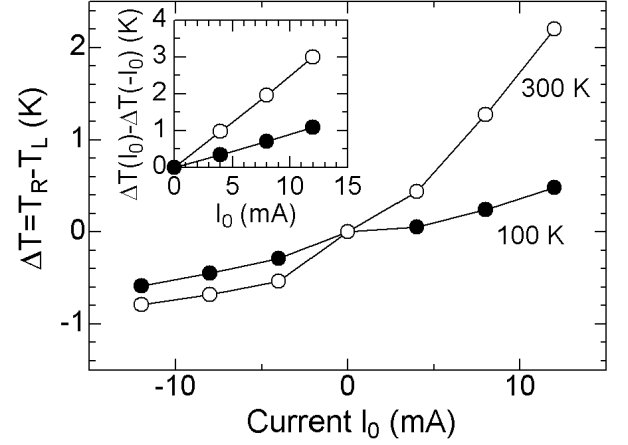

FIG. 3: Temperature difference ΔT as a function of applied current I_0. The inset shows anti-symmetric component of ΔT.

Figure 3 shows the observed ΔT as a function of I_0, which contains a quadratic component of I_0 due to the Joule heating from the misalignment of the thermocouples. In order to cancel the quadratic term, we calculated $\Delta T(I_0) - \Delta T(-I_0)$, which is highly proportional to I_0, as shown in the inset of Fig. 3. We measured several samples to check the experimental accuracy, and found that the obtained κ was reproducible within an error bar of less than 10 % for $Bi_{2-x}Pb_xSr_2Co_2O_y$ and $Ca_3Co_4O_9$, but was rather scattered for Na_xCoO_2.

Figure 4 shows the thermal conductivity of various layered cobalt oxides along the CoO_2 block. As shown in Fig. 4(a), the data for Na_xCoO_2 are scattered from sample to sample. This is partially because Na_xCoO_2 shows a smaller S and weaker Peltier effect than the other cobalt oxides. Another problem is the high contact resistance owing to the chemically active Na layer. Nonetheless we can extract some common features from Fig. 4(a): (i) κ is highest among the three cobalt oxides. (ii) κ decreases with increasing temperature, indicating a phonon-phonon scattering. (iii) The magnitude and temperature-dependence are quite different from those for polycrystalline samples [14, 15]. These features clearly indicate that the disordered Na layer is not very effective for the κ reduction, and that the grain boundary scattering seriously reduces κ of polycrystalline samples.

Figure 4(b) shows κ for $Bi_{2-x}Pb_xSr_2Co_2O_y$ (x=0, 0.4 and 0.6). Unlike Na_xCoO_2, κ decreases with decreasing temperature, and the magnitude is much smaller (particularly for $x = 0$). These results imply that the phonon mean free path is extremely short in $Bi_{2-x}Pb_xSr_2Co_2O_y$. Note that the solid solution between Bi and Pb increases κ, as is opposed to usual cases. The Pb substitution decreases the excess oxygen [17], and removes the superstructure in the Bi-O plane [18]. Thus the Bi-O plane becomes flatter for larger x, which would make phonon
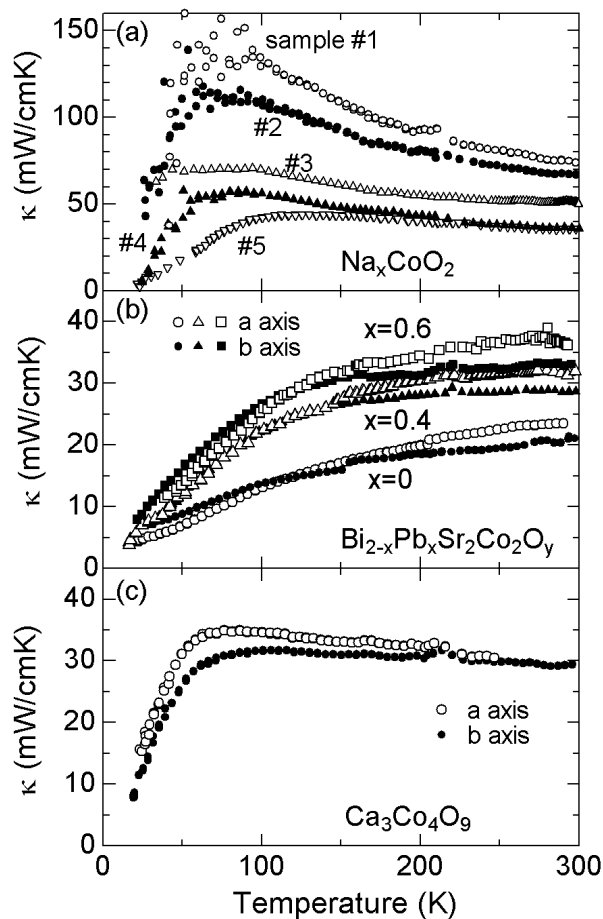
FIG. 4: The in-plane thermal conductivities of the layered cobalt oxides. (a) Na_xCoO_2. Different marks represent different samples (#1-#5). (b) $Bi_{2-x}Pb_xSr_2Co_2O_y$ (x=0, 0.4 and 0.6) and (c) $Ca_3Co_4O_9$. Open and filled symbols represent a- and b-axis thermal conductivity, respectively.

mean free path longer. (The mass difference between Bi and Pb is so small that point-defect scattering due to Pb is negligible.) Another notable feature is that a small but finite anisotropy exists between a and b axes. We think that this is due to the misfit structure between the hexagonal CoO_2 block and the square $Bi_2Sr_2O_4$ block. In fact, we found a large in-plane anisotropy in the resistivity and the thermopower of the same crystals [16].

Figure 4(c) shows κ for $Ca_3Co_4O_9$. As is similar to $Bi_{2-x}Pb_xSr_2Co_2O_y$, a small in-plane anisotropy is observed, which can be attributed to the misfit structure. The magnitude and T dependence are intermediate between those for the previous two systems. Note that a sharp drop below 50 K is clearly observed, which is a hallmark of "clean" crystals. In this sense, the misfit structure does not reduce κ drastically, as was opposed to the theoretical prediction [19].

Let us compare the present data with the previous reports. Funahashi and Shikano [12, 13] reported that the in-plane κ of $Bi_2Sr_2Co_2O_y$ and $Ca_3Co_4O_9$ crystals is 23 and 35 mW/cmK at 300 K, respectively, which is in good agreement with our measurement. This evidences the validity of the Harman method employed here. For Na_xCoO_2, our data are qualitatively consistent with those reported by Fujita et al. [11], but the high κ of Na_xCoO_2 seems overemphasized in their measurement, presumably owing to the high thermal resistance at the Na layer. As mentioned above, the Harman method is free from contact (thermal) resistance, and we believe that the present data are more correct. Very recently, Sales et al. have measured thermal conductivity of single-crystals of Na_xCoO_2, and reported nearly the same value as κ of #2 [20].

Finally we will comment on the physical meaning of the in-plane κ in the layered cobalt oxides. The present study has revealed the following features: (a) Based on the Wiedemann-Franz law, the observed κ is mainly due to phonon contribution. (b) The lower κ tends to show the weaker T-dependence. (c) The lower κ is seen in the material consisting of heavier atoms. One may notice that $Ca_3Co_4O_9$ consisting of lighter atoms has a lower κ than $Bi_{1.4}Pb_{0.6}Sr_2Co_2O_y$. This is perhaps because the Co-O layer in the Ca_2CoO_3 block is highly distorted owing to the misfit structure,[21] and the acoustic phonon mode is less dispersive.

Considering these features, we can conclude that the in-plane κ is mainly determined by the phonons in the charge reservoir block (the block other than the CoO_2 block). This implies that a nano-block integration concept works well in the layered cobalt oxides, where *a nano-block for the electronic part and a nano-block for the thermal part can be independently tuned or designed.* This is a similar situation to the material design for high-temperature superconductors, where a superconductor can be synthesized by combining proper charge reservoirs with the superconducting CuO_2 plane [22]. As a result, we can modify chemical properties, anisotropy and/or unit cell volume, remaining the superconductivity intact. Similarly, we can modify the thermal conductivity by changing the charge reservoir without degrading the large thermopower in the CoO_2 block in the layered cobalt oxides.

In summary, we have measured the in-plane thermal conductivity of the thermoelectric layered cobalt oxides Na_xCoO_2, $Bi_{2-x}Pb_xSr_2Co_2O_y$ and $Ca_3Co_4O_9$, and have found that the charge reservoir block dominates the thermal conduction. By changing the charge reservoir layer, we can modify the thermal properties, remaining the electronic properties in the CoO_2 block unperturbed.

[1] I. Terasaki, Y. Sasago and K. Uchinokura, Phys. Rev. **B56**, R12685 (1997).

[2] For a review, see I. Terasaki, in "*Oxide Thermoelectrics*", edited by K. Koumoto, I. Terasaki, N. Murayama, (Research Signpost, 2002) pp.1-20.

[3] T. Itoh and I. Terasaki, Jpn. J. Appl. Phys. **39**, 6658 (2000).

[4] R. Funahashi and I. Matsubara, Appl. Phys. Lett. **79**, 362 (2001).

[5] Y. Miyazaki, K. Kudo, M. Akoshima, Y. Ono, Y. Koike, and T. Kajitani, Jpn. J. Appl. Phys. **39**, L531 (2000).

[6] A. C. Masset, C. Michel, A. Maignan, M. Hervieu, O. Toulemonde, F. Studer, B. Raveau and J. Hejtmanek, Phys. Rev. **B62**, 166 (2000).

[7] R. Funahashi, I. Matsubara, H. Ikuta, T. Takeuchi, U. Mizutani and S. Sodeoka, Jpn. J. Appl. Phys. **39**, L1127 (2000).

[8] Y. Miyazaki, T. Miura, Y. Ono and T. Kajitani, Jpn. J. Appl. Phys. **41**, L849 (2002).

[9] S. Hebert, S. Lambert, D. Pelloquin and A. Maignan, Phys. Rev. **B74**, 172101 (2001).

[10] A. Maignan, S. Hebert, D. Pelloquin, C. Michel and J. Hejtmanek, J. Appl. Phys. **92**, 1964 (2002).

[11] K. Fujita, T. Mochida and K. Nakamura, Jpn. J. Appl. Phys. **40**, 4644 (2001).

[12] R. Funahashi and M. Shikano, Appl. Phys. Lett. **81**, 1459 (2002).

[13] M. Shikano and R. Funahashi, Appl. Phys. Lett. **82**, 1851 (2003).

[14] K. Takahata, Y. Iguchi, D. Tanaka, T. Itoh and I. Terasaki, Phys. Rev. **B61**, 12551 (2000).

[15] K. Takahata and I. Terasaki, Jpn. J. Appl. Phys. **41**, 763 (2002).

[16] T. Fujii, I. Terasaki, T. Watanabe and A. Matsuda, Jpn. J. Appl. Phys. **41**, L783 (2002).

[17] Y. Morita, J. Poulsen, T. Motohashi, T. Fujii, I. Terasaki, H. Yamauchi and M. Karppinen, submitted to Chem. Mater.

[18] T. Yamamoto, I. Tsukada, K. Uchinokura, M. Takagi, T. Tsubone, M. Ichihara and K. Kobayashi, Jpn. J. Appl. Phys. **39**, L747 (2000).

[19] R. Currat, E. I. Kats and I. Luk'yanchuk, Euro. Phys. J. **B26**, 239 (2002).

[20] B. C. Sales, R. Jin, K. A. Affholter, P. Khalifah, G. M. Veith, and D. Mandrus, cond-mat/0402327.

[21] Y. Miyazaki, M. Onoda, T. Oku, M. Kikuchi, Y. Ishii, Y. Ono, Y. Morii and T. Kajitani, J. Phys. Soc. Jpn. **71**, 491 (2002).

[22] Y. Tokura and T. Arima, Jpn. J. Appl. Phys. **29**, 2388 (1990).